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An essential need of the US Air Force is the discovery, development, and fielding of new, energetic materials for advanced chemical propulsion in space and missile applications. Some of the key factors driving the requirement for new chemical propellants include: (a) improved performance in terms of increased specific impulse and density, (b) reduced sensitivity to external stimuli such as impact, friction, shock, and electrostatic discharge, and (c) mitigation of environmental and toxicological hazards (and the resulting costs) associated with currently used propellants.

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Design of Energetic Ionic Liquids (PREPRINT)

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An essential need of the US Air Force is the discovery, development, and fielding of new, energetic materials for advanced chemical propulsion in space and missile applications. Some of the key factors driving the requirement for new chemical propellants include: (a) improved performance in terms of increased specific impulse and density, (b) reduced sensitivity to external stimuli such as impact, friction, shock, and electrostatic discharge, and (c) mitigation of environmental and toxicological hazards (and the resulting costs) associated with currently used propellants.

A class of compounds which can potentially meet these requirements is known as ionic Liquids (ILs), which are chemical salts with unusually low melting points. The physical and chemical properties of ILs render them useful for many purposes, most notably as environmentally benign ("green") solvents/reaction media but also as catalysts, electrolytes, etc.[1] From a Department of Defense (DoD) perspective, ILs are being explored as new propellants and explosives.[2] The Air Force, in particular, is interested in ILs as potential replacements for currently used monopropellants such as hydrazine – which is carcinogenic, highly toxic, and has relatively modest performance characteristics. In contrast, many ILs have superior densities and specific impulses as well as significantly reduced sensitivity and toxicity characteristics. Furthermore, their properties can be carefully tuned via the choice of the component ions.

The overall objective of the Design of Energetic Ionic Liquids challenge project is to address several key technical issues and challenges associated with the characterization, design, and development of ILs as new monopropellants. Among these, for example, are a fundamental understanding of the (in)stability of ILs, the intrinsic nature of the short- and long-range structure and interactions between the component ions[2e-f], and identification of the key steps in the initial stages of decomposition and combustion[2a-c]. The research described in this article is focused on characterization of the structures and stabilities of ion pair clusters and prediction of their interaction energies in the gas phase.

Our computational approach utilizes quantum chemical methods for prediction of ion pair structures and interaction energies. In particular, geometry optimizations were performed using second-order perturbation theory[3] (MP2, also known as MBPT(2)) with the aug-cc-pvdz basis set[4], denoted as MP2/aug-cc-pvdz. Relative energies were refined using a systematic series of single-point energy calculations at the MP2 and coupled cluster (e.g., singles and doubles with a perturbative estimate of triples, CCSD(T)[5]) levels of theory. Specifically, MP2/cc-pvdz, MP2/aug-cc-pvdz, and CCSD(T)/cc-pvdz energy calculations were combined to obtain estimated CCSD(T)/aug-cc-pvdz relative energies. All computations were performed using the GAMESS quantum chemistry code.[6]

MP2 and coupled cluster (CC) calculations in GAMESS utilize a library of communications routines known as the Distributed Data Interface (DDI),[7] a high-level communications layer operating between GAMESS and the underlying message-passing protocols (Shared Memory (SHMEM), Message Passing Interface (MPI), Low-level Application Programming Interface (LAPI), or sockets within a Transmission Control Protocol/Internet Protocol (TCP/IP) stack.) In

the case of the Naval Oceanographic Office Major Shared Resource Center (NAVO MSRC) IBM systems KRAKEN and BABBAGE, DDI uses MPI for intranode communications and the LAPI protocol for messages between nodes. These types of calculations have significant memory requirements and therefore are well suited for execution on systems with large amounts of memory per node, such as BABBAGE. Coupled cluster calculations are especially memory intensive and, as implemented in GAMESS with DDI, utilize a three-fold hierarchy of memory. First, a modest amount of Replicated Data (RD) is exclusively assigned to each core. Similarly, a block of Node-specific Data (ND) is reserved on each node and is shared by all the cores on that node. The remaining memory on each node is collectively shared by all cores as a large, single pool of Distributed Data (DD). Therefore, the required Memory (M_{CC}) per node for CC calculations is $M_{CC} = P*(RD) + (ND) + (DD)/N$, where "P" and "N" are the number of cores per node and the total number of nodes, respectively, used in the computation.

The values of RD, ND, and DD are determined by the specifics of the calculation, whereas suitable values of P and N are dictated by the hardware; specifically, the amount of accessible physical memory per node. If necessary, P can be chosen to be smaller than the number of available cores per node P_{max} in order to reduce the amount of required memory per node. Table 1 summarizes the memory requirements for CCSD(T) calculations using a series of increasingly large basis sets. Only the smallest calculation (CCSD(T)/cc-pvdz) could be performed within the constraints of the hardware (P_{max} and M_{max}) and the challenge queue limits (N_{max} and T_{max}, see Table 2.) In principle, the CCSD(T)/6-311++G(d,p)[8] and CCSD(T)/aug-cc-pvdz calculations could be run on the pair of "bigmem" nodes, but the estimated required wall time of the former, on the order of 100 days, is prohibitively long. Conversely, this calculation would be within the realm of practicality if ~100 bigmem nodes were available.

One of the specific ion combinations considered in this work is the 1,2,4-triazolium cation ($[C_2N_3H_4]+$) paired with the dinitramide anion ($[N(NO_2)_2]-$). Of the numerous structures found for the two pairs of 1,2,4-triazolium and dinitramide ions, or the pairs of corresponding neutral 1,2,4-triazole and dinitramine molecules, the most stable MP2/aug-cc-pvdz optimized geometries are shown in Figure 1. In the ionic structure, each 1,2,4-triazolium forms two hydrogen bonds, via the hydrogens on the N atoms, to the O atoms of the dinitramide ions. Interestingly, this structure exhibits parallel stacking of the two cationic 1,2,4-triazolium rings. The interplane distance is ~3.2 Å, with a parallel displacement of ~1.4 Å. The corresponding neutral tetramer shows a similar parallel stacking arrangement of the triazole rings.

Furthermore, it is of interest to determine the cluster size at which the ion pair structures become more stable than the corresponding neutral pair structures. A previous study predicted that ion pair dimers are typically higher in energy than neutral pair dimers.[2c] Including zero point vibrational energy (ZPVE) corrections, the ionic tetramer in Figure 1 is 1.2 kilocalorie / mole (kcal/mol) lower than that of the neutral one. The MP2 method tends to predict higher energies for ionic species vs. neutral species,[2c] so more accurate CCSD(T)/aug-cc-pVDZ energy calculations of these two tetramer structures were desired. However, since the computational cost of CCSD(T)/aug-cc-pVDZ is prohibitive, these energies were approximated from the MP2/aug-cc-pVDZ energies by estimating the electron correlation energy differences using three independent methods: (1) the differences between the MP2/cc-pVDZ and CCSD(T)/cc-pVDZ energies of the tetramers, (2) the differences between the MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVDZ energies of the twelve pairs of dimers in these two tetramers, and (3) the differences between the MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVDZ energies of the eight monomers in

these two tetramers. Using these three methods, and including ZPVE corrections, the estimated CCSD(T)/aug-cc-pVDZ energy of the ionic tetramer is lower than that of the neutral tetramer by 5.7, 7.3, and 7.7 kcal/mol, respectively.

In conclusion, quantum chemical calculations suggest that cation-cation parallel stacking structures can exist in very small ionic clusters such as two 1,2,4-triazolium cations and two dinitramide anions. Furthermore, for two pairs of 1,2,4-triazolium and dinitramide, ionic structures are more stable than the corresponding neutral structures. Finally, it should be noted that lower theoretical methods which do not include the effects of electron correlation, such as Hartree-Fock, do not predict a parallel stacking geometry of the rings. Therefore, it is essential to utilize correlated methods such as MP2 and CCSD(T) in order to obtain proper descriptions of the structures and interaction energies of these ion clusters. The structural motifs and interaction patterns found in this study provide new understanding of ionic materials with aromatic rings.

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Table 1. Memory requirements for CCSD(T) single point energy calculations.[a]

Basis set (# of AOs)	RD (MW/core)	ND (MW/node)	DD (MW)	P	N	MCC (MW/node)
cc-pvdz (376)	8	1175	4950	16	64	1,381
6-311++G(d,p) (580)	22	3298	16,000	16	64	3,900b
				1	64	3,570b
				16	2	11,474c
aug-cc-pvdz (622)	26	3,875	19,150	1	64	4,200b
				1	2	13,476c
aug-cc-pvtz (1268)	330	18,493	146,000	1	64	21,105b
				1	2	91,823d
aug-cc-pvqz (2228)	2495	60,370	807,000	1	64	75,475b
				1	2	466,365d

a "MW" denotes megawords (106 64-bit words.)

b Exceeds amount of usable physical memory on each standard node (see Table 2.)

c Fits within usable physical memory on each bigmem node, but execution time is prohibitively long.

d Exceeds amount of usable physical memory on each bigmem node (see Table 2.)

Table 2. Challenge and bigmem queue characteristics on babbage.a

Queue	Cores per node (Pmax)	Maximum # of nodes (Nmax)	Maximum memory/node Mmax (MW/node)	Maximum wall time Tmax (hours)
challenge	16	64	~3,500	48
bigmem	16	2	~15,500	48*

a "MW" denotes megawords (106 64-bit words.)

* 48 hour limit obtained via special request. The default wall time limit of the bigmem queue is 12 hours.
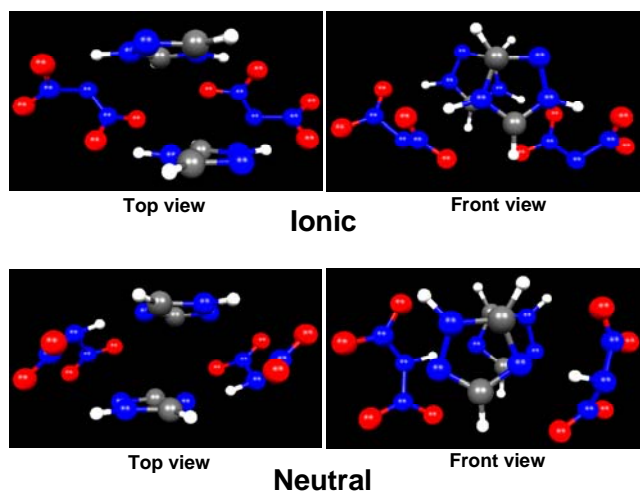

Figure 1. MP2/aug-cc-pVDZ optimized structures of two pairs of 1,2,4-triazolium (1,2,4-triazole) and dinitramide (dinitramine) molecules. H is white, C is gray, O is red, N is blue.